

Synthesis, characterization, kinetic and thermodynamic evaluation from TG-DTA analysis of new nickel(II) mixed ligand complexes of bidentate salicylaldimine Schiff bases and 1,10-phenanthroline

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New mixed-ligand complexes of nickel(II) ion with bidentate salicylaldimine ligands $\{[(2\text{-carboxyphenyl)imino)methyl}\}$ phenol; (L^1), $\{[(2\text{-hydroxyphenyl)imino)methyl}\}$ phenol (L^2), $\{[(2\text{-chlorophenyl)imino)methyl}\}$ phenol; (L^3) and $\{[(3\text{-methyl-2-chlorophenyl)imino)methyl}\}$ phenol; (L^4) with 1,10-phenanthroline; (L^5) were prepared by reacting NiCl_2 at an appropriate mole ratio of these ligands. The complexes were characterized by FT-IR, UV-Visible, ^1H NMR spectra, conductivity measurements and thermal analysis. The spectral data indicated that the salicylaldimine ligand is a monobasic bidentate ligand coordinated through NO donor atoms and 1,10-phenanthroline is a neutral bidentate ligand coordinated through NN donor atoms to the nickel(II) ion. The prepared complexes seem to have octahedral geometry of the general formula $[\text{NiL}^x(\text{L}^5)_2]\text{Cl}$ ($x=1-4$). The thermal behavior of the prepared compounds was studied using thermogravimetric (TG/DTA) analysis in static air. The obtained results show a continuous weight loss without any hydrated or coordinated water molecule losses, and the ligand molecules immediately decompose in consecutive steps.

Keywords: Schiff bases, Bidentate salicylaldimine ligand, Neutral bidentate ligand, Nickel(II) mixed ligand complex, Octahedral geometry complex, Thermogravimetric analysis.

INTRODUCTION

The complexes of mixed ligands have been widely investigated in solution and solid state [1]. Schiff bases and their metal complexes demonstrate a range of applications varying from catalysis to pharmaceuticals [2, 3]. The ternary transition metal complexes including an aromatic Schiff base and 1,10-phenanthroline have been extensively studied [4]; they are more stable compared with binary complexes so the steric effect and back donation have to be considered in defining the structure of the mixed ligand complexes [1]. Many studies have been done on the physico-chemical properties of various symmetrical Schiff bases and their transition metal complexes [5, 6], while few were done for the complexes of asymmetric Schiff bases and chelates with 1,10-phenanthroline, pyridine, and 2,2'-bipyridine ligands. The coordination of transition metals to different Schiff bases gives a series of novel complexes possessing a broad spectrum of bioinorganic applications and thermal stability [7], therefore a lot of mixed-ligand complexes including Schiff bases with heterocyclic bases have been reported due to their ability to enhance the biological activity and decrease the cytotoxicity of both the ligand and the metal ion on the host body [8, 9].

In this work, we report the synthesis, characterization and comparison of the thermal

decomposition behavior of the mixed ligand complexes of Ni(II) ion with salicylaldimine and 1,10-phenanthroline as bidentate ligands. The activation energy E_a and the thermodynamic parameters ΔS^* , ΔH^* and ΔG^* of the activated complexes were calculated by using the differential Freeman-Carroll equation. The molar conductivities show that the prepared complexes display electrolytic behavior due to the presence of one chloride ion outside of the coordination sphere [10].

EXPERIMENTAL

Materials

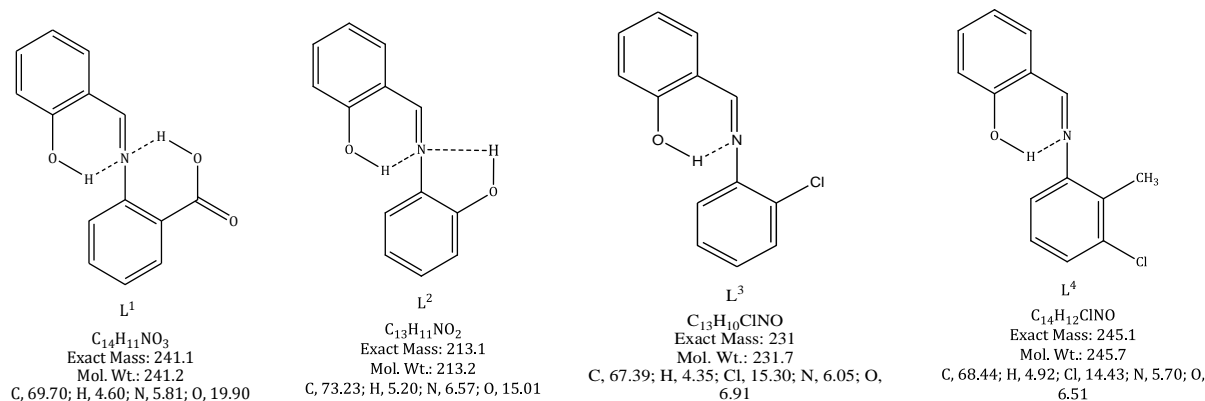
The starting materials were purchased from Fluka Chemicals Company and were used without further purification.

Synthesis of Schiff base ligands

The Schiff bases were prepared according to [11], by mixing 1.1 g, 1 mol of salicylaldehyde in 10 ml of ethanol with an equimolar quantity of substituted aniline, magnetically stirred with adding 2-3 drops of concentrated sulfuric acid, refluxed for 2 h and let overnight at room temperature. The obtained product was collected, recrystallized from hot ethanol, washed with ether and dried under vacuum at room temperature, Scheme 1.

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Scheme 1. The chemical structures of the ligands

Synthesis of complexes

The nickel(II) complexes were prepared as described in [11], by mixing an ethanolic solution of appropriate molar quantity of a Schiff base ligand (L^x ; $x=1-4$), 10 mmol with an ethanolic solution of Ni(II) chloride 10 mmol and refluxed for 3 h. To the mixture, an ethanolic solution of 1,10-phenanthroline 20 mmol was added and refluxed for an additional 1 h. The obtained product was collected, washed with ethanol, ether and dried under vacuum at room temperature.

Thermal study

TG/DTG of the four Schiff base ligands (L^x ; $x=1-4$) and their nickel(II) mixed ligand complexes with 1,10-phenanthroline were carried out to evaluate the thermal stability and characteristic parameters from the analysis of their thermograms.

RESULTS AND DISCUSSION

Infrared spectroscopy

Table 1. FT-IR spectral data (cm^{-1}) of the prepared compounds.

Compound	Ar-CH	CH=N	C-O	C=C
L^1	3070	1631	1246	1564
$[NiL^1(L^5)_2]Cl$	3076	1593	1240	1545
L^2	3047	1631	1274	1529
$[NiL^2(L^5)_2]Cl$	3059	1608	1290	1531
L^3	3066	1612	1276	1571
$[NiL^3(L^5)_2]Cl$	3055	1606	1295	1529
L^4	3075	1612	1276	1566
$[NiL^4(L^5)_2]Cl$	3050	1606	1327	1531

The FT-IR spectra of the prepared Schiff base ligands and their nickel(II) mixed ligand complexes

showed sharp and characteristic bands, as summarized in Table 1.

All Schiff base ligands (L^x ; $x=1-4$) show a medium intensity band at 1246, 1274, 1276 and 1276 cm^{-1} , respectively, due to $\nu(C-O)$ stretching frequency, which was shifted to higher frequency at 1260, 1290, 1295 and 1327 cm^{-1} , respectively, in the spectra of the complexes, indicating the coordination partnership of the oxygen atom [11, 12]. The high-intensity bands at 1620, 1631, 1612 and 1614 cm^{-1} , respectively, due to the azomethine group, were shifted to a lower frequency in the spectra of the complexes at 1593, 1612, 1604 and 1606 cm^{-1} , respectively, indicating the coordination of azomethine nitrogen atom to the central metal [14]. In addition, the $\nu(C-N)$ bending band of the 1,10-phenanthroline ligand that appeared at 1158 cm^{-1} was shifted to 1149-1153 cm^{-1} in the spectra of the complexes, indicating the coordination of the pyridine nitrogen atoms of 1,10-phenanthroline ligand to the central metal too [7]. Moreover, the spectra of the complexes showed new bands at 215-255 cm^{-1} due to $\nu(M-N)$ of 1,10-phenanthroline; L^5 and new bands at 420-432 cm^{-1} due to $\nu(M-N)$ and at 467-470 cm^{-1} due to $\nu(M-O)$ vibrations of the Schiff base ligands [15], these bands are out of the scale of the used instrument. So, it is easy to summarize that the salicylaldehyde Schiff base ligands are mononegative bidentate ligands and were coordinated to the nickel(II) ion *via* the phenolic oxygen atom and azomethine nitrogen atom, whilst the 1,10-phenanthroline ligand is a neutral bidentate ligand and was coordinated to the nickel(II) ion *via* its two pyridine nitrogen atoms, see Figs. 1, 2.

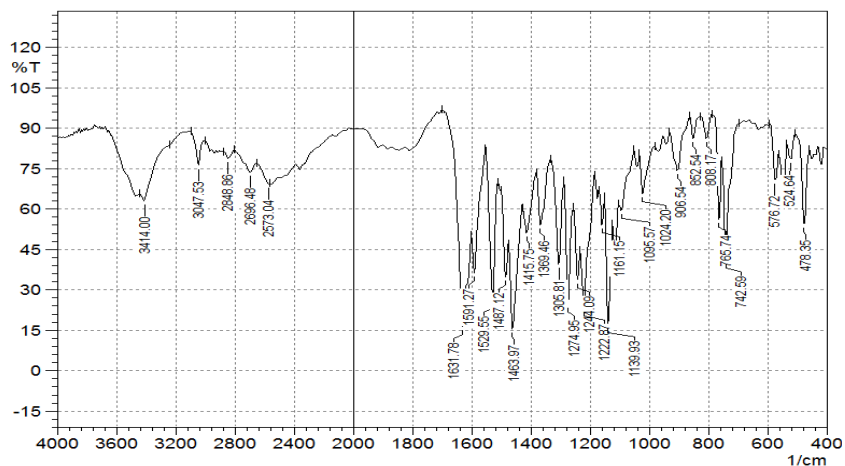


Figure 1. FT-IR of the ligand L².

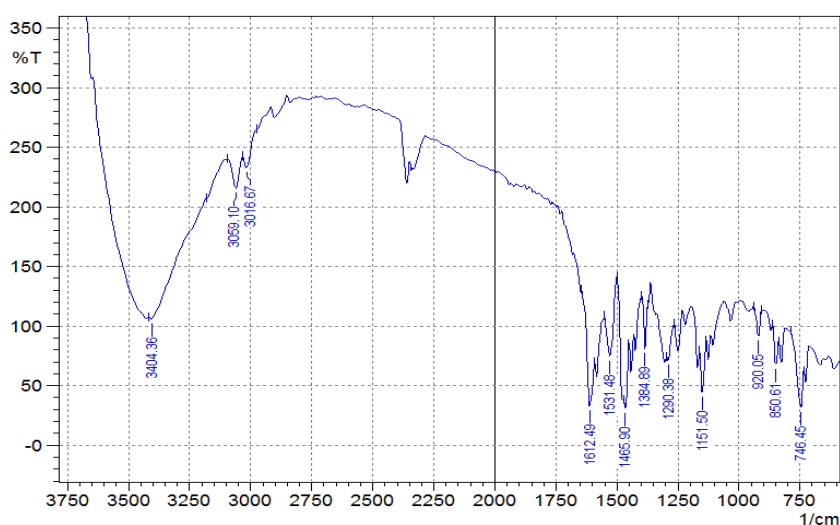


Figure 2. FT-IR of [NiL²(L⁵)₂]Cl complex.

Electronic spectra

The absorption band assignments of the Schiff base ligands (L^x; x=1-4) and of the nickel(II) mixed ligand complexes were clarified in three essential bands in the UV. region, see Figs. 3, 4.

The π - π^* transition of the imine group for the Schiff base ligands appears in the range of 225-272 nm. The π - π^* transition of the aromatic system for the ligands appears in the range of 255-325 nm and the n - π^* transition appears in the range of 335-420 nm, which were significantly affected by chelating [16]. The shifting of the n - π^* transition upon complexation may be attributed to charge transfer from the nitrogen or oxygen atoms of the ligands to the nickel(II) ion [17]. The electronic spectra of the present nickel(II) mixed ligand complexes showed three bands at 268-272 nm, 340-346 nm, and 420-446 nm, respectively, according to the three allowed transitions of the octahedral d^8 system in the ³F ground state [11], Scheme 2.

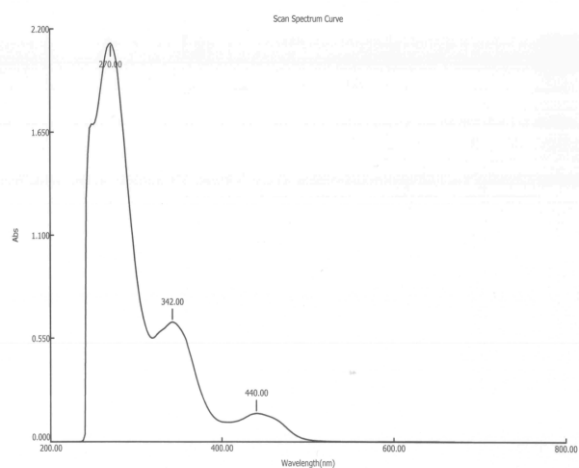


Figure 3. The UV spectrum of [NiL³(L⁵)₂]Cl.

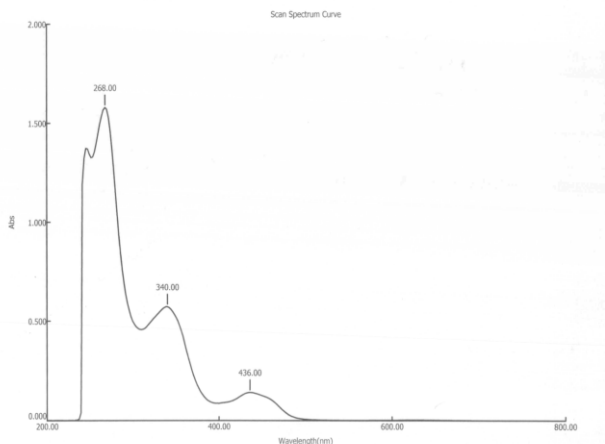
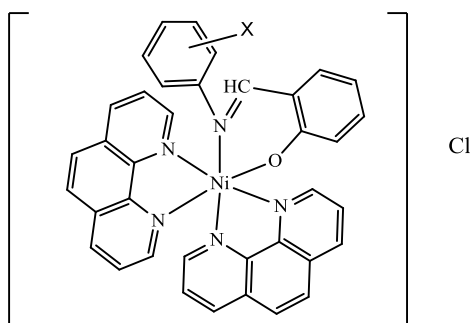


Figure 4. The UV. spectrum $[\text{NiL}^4(\text{L}^5)_2]\text{Cl}$ complexes.



X=L¹: 2-COOH, L²: 2-OH, L³: 2-Cl, L⁴: 2-CH₃-3-Cl

Scheme 2. The suggested octahedral structure of the prepared nickel(II) complexes, $[\text{NiL}^x(\text{L}^5)_2]\text{Cl}$, (x=1-4).

¹H NMR spectroscopy provides more information beside the identification groups in the structure of Schiff base ligands and nickel(II) mixed ligand complexes, showing an expected protons ratio, which is in agreement with previous work [6, 18]. The ¹H NMR spectra of Schiff base ligands (L^x; x=1-4) in DMSO-d⁶ (Fig. 5) display a distinctive signal at 8.96-10.25 ppm attributed to azomethine protons, which shifted downfield for the nickel(II) complexes, confirming the coordination of metal ion to the azomethine [14].

The phenolic protons always have a high chemical shift value δ , which confirms the intramolecular hydrogen bonding with the adjacent nitrogen atom [19]. The signals observed at 10.70-13.77 ppm are due to the phenolic -OH of the ligands. The multiple signals assigned to the aromatic protons of both rings were not affected by complexation. The number of peaks and the proton resonance of the Schiff base ligands completely differ upon complexation. The absence of proton signals of phenolic -OH and the downfield shift of the resonance of azomethine proton confirm the metal coordination with a phenolic oxygen atom and azomethine nitrogen atom of the Schiff base ligands [20].

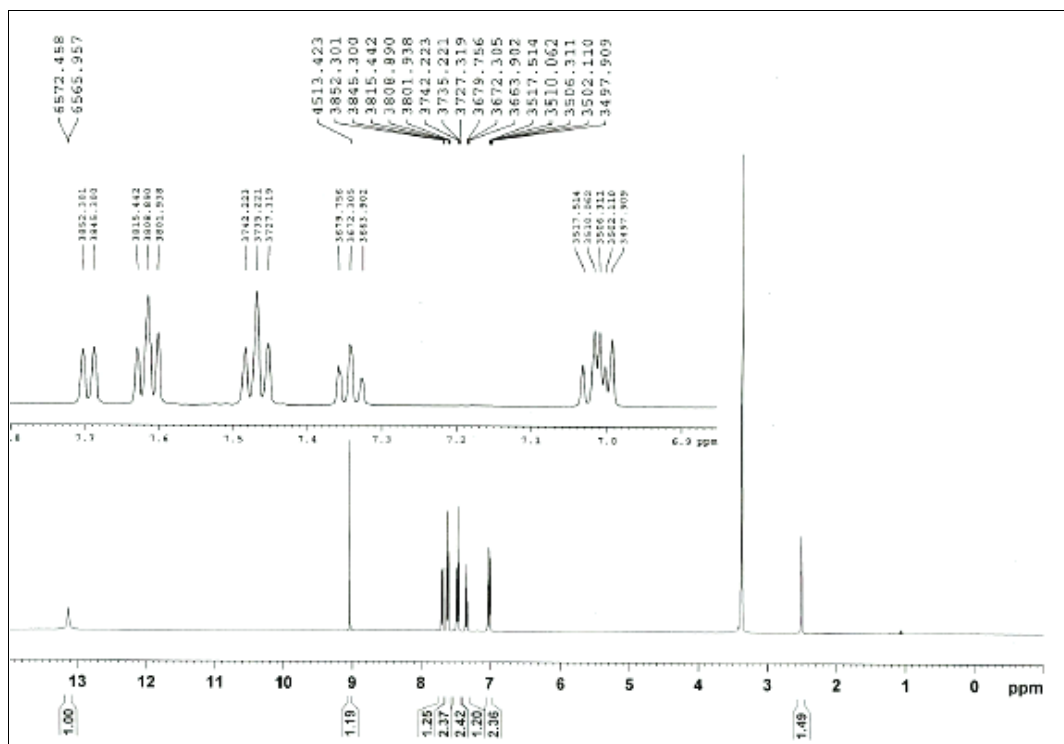


Figure 5. ¹H NMR spectra of the L³ ligand.

Thermal analysis

TG and DTA were used in this work as thermoanalytical methods to investigate the thermal stability, kinetic and thermodynamic characteristic parameters, see Figs. 6-14.

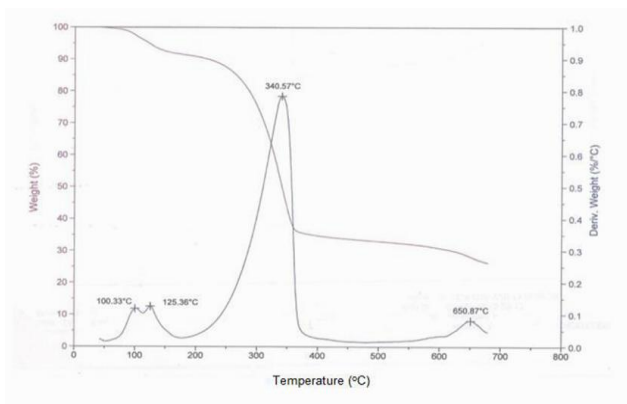


Figure 6. TG and DTA of L^5 .

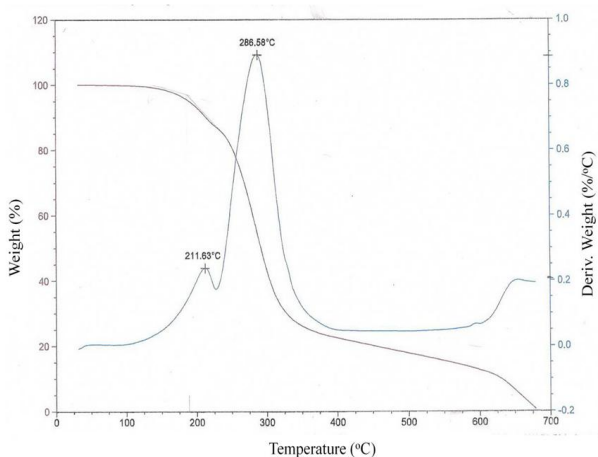


Figure 7. TG and DTA of L^1 .

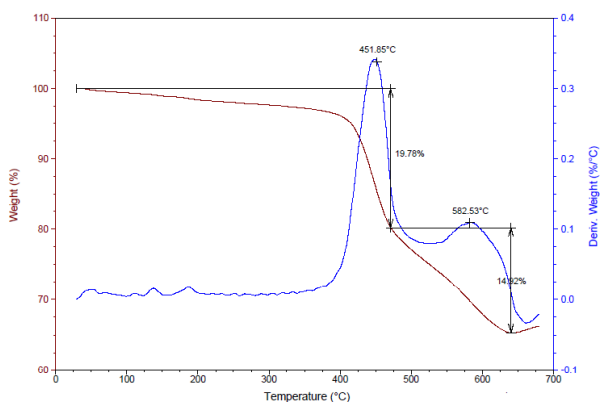


Figure 8. TG and DTA of $[NiL^1(L^5)_2]Cl$ complex.

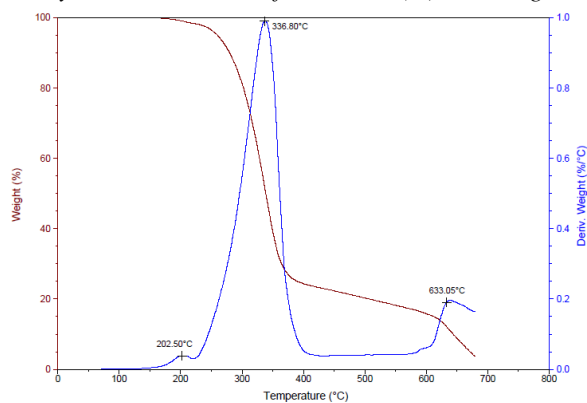


Figure 9. TG and DTA of L^2 .

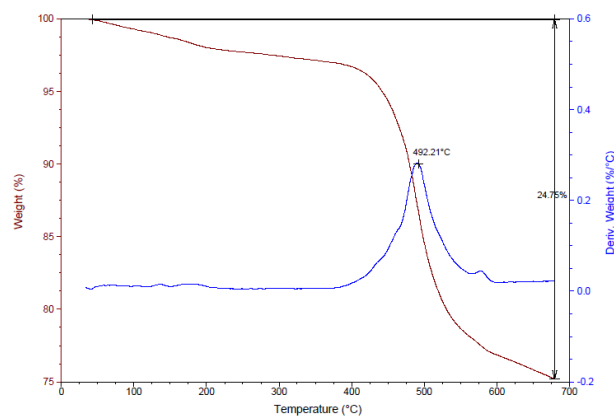


Figure 10. TG and DTA of $[NiL^2(L^5)_2]Cl$ complex.

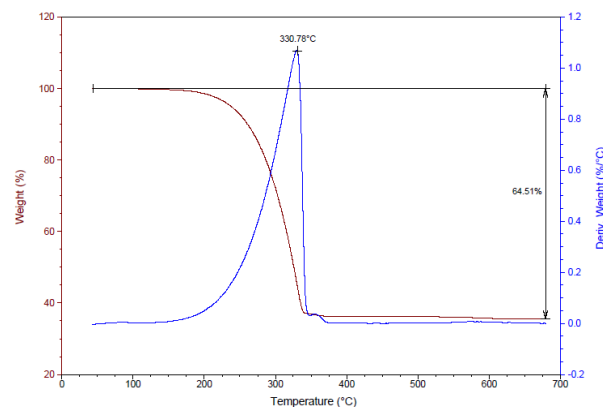


Figure 11. TG and DTA of L^3 .

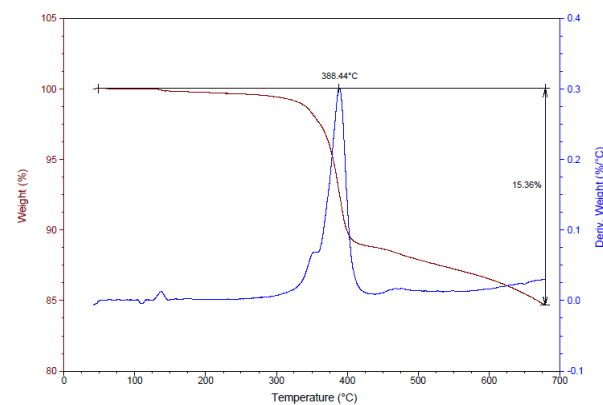


Figure 12. TG and DTA of $[NiL^3(L^5)_2]Cl$ complex.

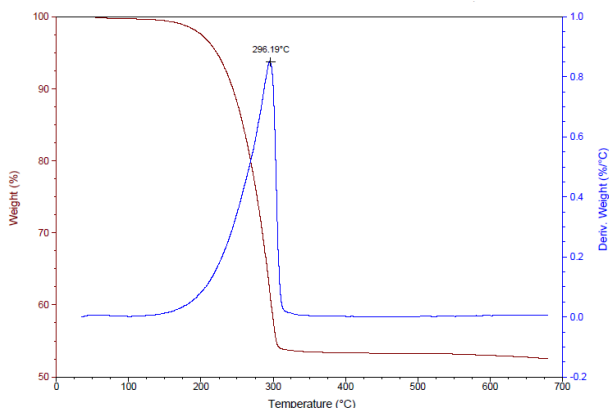


Figure 13. TG and DTA of L^4 .

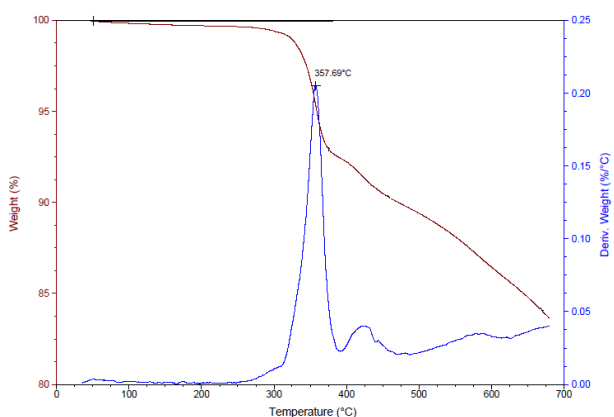


Figure 14. TG and DTA of $[NiL^4(L^5)_2]Cl$ complex.

The TG curves were mathematically analyzed by the differential Freeman-Carroll equation [21]. The kinetic parameters like activation energy; E_a for the dehydration and decomposition of 1,10-phenanthroline, Schiff base ligands and their nickel(II) complexes were calculated from the Arrhenius plot of the rate of decomposition; $\ln k$ versus $1/T_s$, E_a was calculated from the slope and the frequency factor; Z was defined from the obtained intercept. The thermodynamic parameters of the activated complexes are often calculated using the following equations:

$$\Delta S^* = 2.303 \log \left[\frac{Z h}{k_B T_s} \right] R$$

$$\Delta H^* = E_a - RT_s$$

$$\Delta G^* = \Delta H^* - T_s \Delta S^*$$

The peak temperature T_s is used in these calculations so that the values of ΔS^* , ΔH^* and ΔG^* are related to the highest rate of the process, as summarised in Table 2.

The negative values of ΔS^* indicate that the decomposition reactions proceed spontaneously and the low values of Z indicate that they were slow reactions in their nature [22]. According to the TG analysis, both the stability and decomposition temperature of the complexes were higher than those of the ligands. Usually, on pyrolysis the Schiff base complexes suffer volatilization leaving

a modest residue or decomposition to metal oxide [23].

The thermal decomposition process of the $[NiL^x(L^5)_2]Cl$ complexes involves two, one, one and three distinguished decomposition steps, respectively. The thermograms of these complexes point to their thermal stability up to 376, 426, 326 and 313 °C, respectively, indicating no moisture and solvent residue in these complexes. This fact was confirmed by the absence of the endothermic peak in 150-200 °C region of the DTA curves [24]. The sharp step due to the ligands decomposition takes place in the temperature range of 526-656, 426-559, 326-420 and 313-390 °C, respectively. Horizontal thermal curves were observed at 700-1000 °C. The percent weight of the residue corresponds to NiO as end product [25], Table 3. The relative thermal stability of the complexes is $3 < 4 < 1 < 2$ according to the decomposition temperature, while the E_a and Z values for the complexes are $1 < 2 < 3 < 4$ according to the crucial kinetic standards, which mostly differ from those defined by the thermal stability. The results of the thermal studies revealed that the complexes were more stable than the ligands through the thermal decomposition temperature by employing the formation of M-N and M-O coordination bond between the ligand and Ni(II) ion.

CONCLUSION

We have described the synthesis, spectroscopic and thermal properties of new nickel(II) mixed ligand complexes. The chemical structures were suggested based on FT-IR, UV-Visible, 1H NMR spectra, conductivity measurements and thermal analysis. The octahedral geometry of the general formula $[NiL^x(L^5)_2]Cl$ ($x=1-4$) was confirmed. The thermal properties of the prepared complexes were determined by thermogravimetric (TG/ DTA) analysis in static air and different thermodynamic parameters were obtained by using Freeman-Carroll equation.

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Table 2. Thermal stability and thermodynamic parameters of ligands (L^x , $x=1-4$, L^5) and nickel complexes $[NiL^x(L^5)_2]Cl$.

Compound symbol	w_0 (mg)	T_s (k)	Temp. of 50% wt loss $^{\circ}C$	Rate of decomp. (%/min)	Chare cont. 625 $^{\circ}C$ (%)	Act. energy (E_a) (KJ/mol)	Temp. range ($^{\circ}C$)	Z	ΔH^* KJ/mol	ΔS^* KJ/mol	ΔG^* KJ/mol
L^1	20.3490	559.58	295	27.6	10.4	38.29	89-220	0.001	33.64	-305.75	171.13
$[NiL^1(L^5)_2]Cl$	22.7160	724.85	----	13.33	66	32.64	150-404	0.007	26.61	-312.138	226.2
L^2	39.365	609.80	337.04	29.62	14.19	62.88	180-263	0.015	57.76	-285.35	174.07
$[NiL^2(L^5)_2]Cl$	18.2870	765.21	----	7.6	76.33	38.29	203-433	0.038	31.9	-279.97	214.27
L^3	28.970	603.78	323.31	29.44	36.01	109.69	199-246	0.005	104.67	-294.87	178.17
$[NiL^3(L^5)_2]Cl$	16.1280	661.44	-----	7.56	85.99	100.33	246-344	0.023	94.83	-282.92	187.23
L^4	23.1980	589.19	-----	20.62	53.33	114.88	168-210	0.015	110.15	-285.31	76.917
$[NiL^4(L^5)_2]Cl$	20.2290	630.69	----	2.18	85.67	182.1	283-333	0.084	176.85	-271.75	171.57
L^5	24.1520	613.57	342.3	27.47	30.67	83.77	154-263	0.891	78.67	-271.04	166.39

Table 3. Thermoanalytical results TG and DTA of Ni(II) mixed ligand complexes.

Complex	Mwt	Initial wt w_0 (mg)	TG range ($^{\circ}C$)	Temp. of decomp. ($^{\circ}C$)	Mass loss estimation (calc.)%	Total mass loss estim. (calc.)%	Assignment	Residue (1000 $^{\circ}C$)
$[NiL^1(L^5)_2]Cl$ $C_{38}H_{26}ClN_5NiO_3$	694.8	22.716	376-526 526-656	451.81 582.51	19.78 (19.79) 14.92 (14.53)	34.70 (34.32)	$C_4H_8NO_2Cl$ and $C_{2.5}H_{11}N_4$	NiO+31.5C
$[NiL^2(L^5)_2]Cl$ $C_{37}H_{26}ClN_5NiO_2$	666.8	18.287	426-566	492.21	24.75 (25.71)	24.75 (24.71)	$C_2H_2ClN_5O$	NiO+35.5C
$[NiL^3(L^5)_2]Cl$ $C_{37}H_{25}Cl_2N_5NiO$	685.2	16.128	326-420	388.4	24.30 (24.22)	24.30 (24.22)	$H_{25}Cl_2N_5$	NiO+37C
$[NiL^4(L^5)_2]Cl$ $C_{38}H_{27}Cl_2N_5NiO$	699.3	20.229	313.5-390 390-476 476-630	357.69 425 583.25	10.45 (10.43) 5.06 (5.00) 8.60 (8.58)	24.11 (24.01)	$H_{27}Cl_2N_2$	NiO+38C

REFERENCES

1. D. Banerjee, Mixed-ligand complexes in coordination chemistry, New Delhi, Tata McGraw-Hill Publishing company Limited, 1993.
2. V. P. Daniel, B. *Spectrochim. Acta Part A*, **70**(2), 403 (2008).
3. N. G. Kandile, M. I. Mohamed, H. M. Ismaeel, *J. Enzyme Inhib. Med. Chem.*, **32**(1), 119 (2017).
4. M. A. Diab, A. Z. El-Sonbati, A. A. El-Bindary, S. M. Morgan, M. K. Abd El-Kader, *J. Mol. Liq.*, **218**, 571 (2016).
5. J. C. Lee, Y. K. Jeong, J. M. Kim, J. G. Kang, *Spectrochim. Acta Part A*, **124**, 256 (2014).
6. G. G. Mohamed, M. M. Omar, A. A. Ibrahim, *Eur. J. Med. Chem.*, **44**(12), 4801 (2009).
7. H. F. A. El-Halim, G. G. Mohamed, E. A. M. Khalil, *J. Mol. Struct.*, **1146**, Suppl. C, 153 (2017).
8. G. B. Bagihalli, P. G. Avaji, S. A. Patil, P. S. Badami, *Eur. J. Med. Chem.*, **43**(12), 2639 (2008).
9. A. K. Patra, M. Nethaji, A. R. Chakravarty, *J. Inorg. Biochem.*, **101**(2), 233 (2007).
10. W. J. Geary, *Coord. Chem. Rev.*, **7**(1), 81 (1971).
11. Y. Prashanthi, K. Kiranmai, I S. Kumar, V. K. Chityala, Shivaraj, *Bioinorg. Chem. Appl.*, 948534, 1 (2012).
12. K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, 5th edn. New York, John Wiley and Sons, 1998.
13. H. F. Abd El-halim, M. M. Omar, G. G. Mohamed, *Spectrochim. Acta Part A*, **78**(1), 36 (2011).
14. P. P. Utthra, G. Kumaravel, N. Raman, *J. Mol. Struct.*, **1150**, 374 (2017).
15. G. G. Mohamed, M. M. Omar, A. M. M. Hindy, *Spectrochim. Acta Part A*, **62**(4), 1140 (2005).
16. S. Samal, R. R. Das, R. K. Dey, S. Acharya, *J. Appl. Polym. Sci.*, **77**(5), 967 (2000).
17. S. Samal, N. K. Mohapatra, S. Acharya, R. K. Dey, *React. Funct. Polym.*, **42**(1), 37 (1999).
18. W. H. Mahmoud, G. G. Mohamed, M. M. I. El-Dessouky, *J. Mol. Struct.*, **1082**, 12 (2015).
19. S. M. Lee, H. M. Ali, K. S. Sim, S. N. Abdul Malek, K. M. Lo, *Inorganica Chim. Acta*, **406**, 272 (2013).
20. R. Narain, *Res. J. Chem. Sci.*, **2**(4), 231 (2012).
21. L. Vlaev, N. Nedelchev, K. Gyurova, M. Zagorcheva, *J. Anal. Appl. Pyrolysis*, **81**(2), 253 (2008).
22. R. L. Blaine, H. E. Kissinger, *Thermochim. Acta*, **540**, 1 (2012).
23. M. Ikram, S. Rehman, Faridoon, R. J. Baker, H. U. Rehman, A. Khan, M. I. Choudhary, S. U. Rehman, *Thermochim. Acta*, **555**, 72 (2013).
24. S. Ilhan, H. Baykara, A. Oztomsuk, V. Okumus, A. Levent, M. Salih Seyitoglu, S. Ozdemir, *Spectrochim. Acta Part A*, **118**, 632 (2014).
25. M. H. Soliman, G. G. Mohamed, *Spectrochim. Acta Part A*, **91**, 11 (2012).